Columnar mesophases from nondiscoid luminescent mesogens containing 1,3,4-oxadiazole

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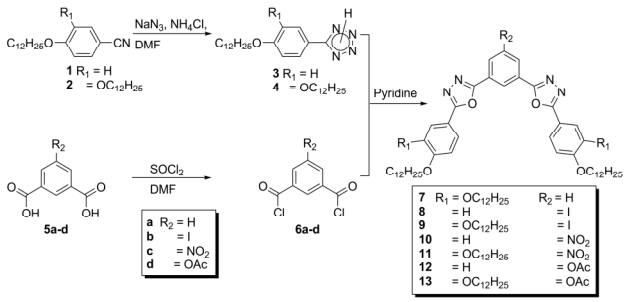
Keywords: 1,3,4-oxadiazoles, luminescence, columnar mesophases

INTRODUCTION

Discotic liquid crystals (DLCs) are typically described as disc-shaped molecules with rigid aromatic core and flexible peripheral chains.[1] However, many nondiscoid molecules such as half-disc shaped have been studied considerably in an attempt to develop new types of core architecture for forming columnar mesophases.[2] Heterocyclic oxadiazoles have been extensively studied for a long time due to their high thermal and chemical stability and high photoluminescence quantum yield.[3] Derivatives of this heterocycle are strong candidates for technological applications, particularly as emitters for optical devices or charge transporters for OLEDs.[4] In this work, the synthesis of a new class of nondiscoid mesogens containing 1,3,4-oxadiazole and the study regarding the relationship between chemical structure and mesomorphic behavior, thermal and optical properties is reported

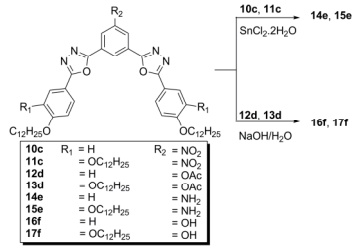
RESULTS AND DISCUSSION

Firstly, 1,3-dipolar cicloaddition of NH_4N_3 (prepared *in situ,* from NaN_3 and NH_4Cl), to nitriles **1** and **2** furnished the tetrazoles **3** and **4**. Compound (**7**-**13**) were obtained by a Huisgen reaction using **3** or **4** and the freshly prepared acid dichloride **6a-d** in dry pyridine under reflux, affording the final compounds **7**-**11** in 58-92 % (Scheme 1).



Scheme 1. Synthesis of compounds **7-13**.

Compounds **12d** and **13d** were not isolated, and the deprotection was performed, *in situ*, with $NaOH_{aq}$, resulting the compounds **16f** and **17f** (Scheme 2) in 52 and 70 % yields, respectively. The compounds **14e** and **15e** were prepared from **10c** and **11c** *via* reduction of the nitro group by $SnCl_2$, yielding 90 and 97 %, respectively.



Scheme 2. Synthesis of final products **14-17**.

The structures of all the compounds were characterized by IR and ^1H and ^{13}C NMR spectra and elemental analysis. The mesomorphic properties of the final compounds were investigated by POM, DSC, and TGA. The mesophase were characterized by POM and DSC as Smectic A phases for **10c**, hexagonal columnar phase (Col_h) for the compounds **11c**, **15e, 16f** and **17f** which were confirmed by XRD analysis. The photophysical properties of final compounds, in solution and in solid state, were evaluated, and displayed blue fluorescence (2-64%) in $CHCl_3$ solution and with large Stoke's shifts (59-92 nm). The compounds presented great thermal stability (313-410 ℃).

CONCLUSION

Design and synthesis of a new class of 1,3,4-oxadiazole heterocycles were reported in this study. Five of the ten molecules are liquid crystals. Their ability to form Col_h, despite their half-disc shape may be explained by the formation of antiparallel arrangement which have been observed by XRD analysis. These compound have luminescent liquid crystals properties and were obtained in good yields.

ACKNOWLEDGEMENTS

UFSC, CNPq, SBQ, FAPESC and INCT catálise.

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